

**SETTING AND CURING ACCELERATOR FOR HYDRAULIC BINDERS
AND PROCESSES FOR PRODUCING IT**

Technical field

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The invention relates to a setting and curing accelerator for hydraulic binders according to the preamble of the first claim.

10 The invention likewise relates to a process for producing a setting and curing accelerator for hydraulic binders according to the preamble of the independent process claim.

Prior art

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Many substances which accelerate the setting and curing of concrete are known. Customary substances are, for example, strongly alkaline substances such as alkali metal hydroxides, alkali metal carbonates, alkali metal silicates, alkali metal aluminates and alkaline earth metal chlorides. However, the strongly alkaline substances have undesirable effects on the processor, e.g. burns, and they reduce the final strength and durability of the concrete.

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EP 0 076 927 B1 discloses alkali-free setting accelerators for hydraulic binders which are said to avoid these disadvantages. To accelerate the setting and curing of a hydraulic binder such as cement, lime, hydraulic lime and plaster of Paris and mortar and concrete produced therefrom, from 0.5 to 10% by weight, based on the weight of this binder, of an alkali-free setting and curing accelerator comprising aluminum hydroxide is added to the mixture comprising the binder mentioned.

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Such mortars and concretes are particularly well-suited as spray mortar and concrete as a result of the

accelerated setting and curing.

EP 0 946 451 B1 discloses setting and curing
accelerators in dissolved form for hydraulic binders,
5 which can be more easily mixed into the concrete when
spraying the concrete. Such a setting and curing
accelerator comprises, inter alia, aluminum hydroxide,
aluminum salts and organic carboxylic acids. However, a
disadvantage of such setting and curing accelerators is
10 the stability of the solution.

Summary of the invention

It is an object of the invention to achieve a very high
15 accelerating action combined with a very long life of
the accelerator for a setting and curing accelerator
for hydraulic binders of the type mentioned at the
outset.

20 According to the invention, this is achieved by the
features of the first claim.

The advantages of the invention are, inter alia, that a
high stability, i.e. stabilization of the accelerator
25 solution, is achieved by means of the accelerators of
the invention and that high acceleration of the setting
and curing of hydraulic binders is achieved.

Hydraulic binders with addition of the accelerator of
30 the invention can be processed advantageously by
spraying because of their accelerated setting and
curing behavior.

Further advantageous embodiments of the invention are
35 disclosed in the subordinate claims.

Way of carrying out the invention

A setting and curing accelerator according to the invention for hydraulic binders comprises:

- 5 $\text{Al}_2(\text{SO}_4)_3$ aluminum sulfate, $\text{Al}(\text{OH})_3$ aluminum hydroxide and mineral acid in aqueous solution.

Such a setting and curing accelerator according to the invention advantageously consists essentially of (in %
10 by weight):

- 10-50% of $\text{Al}_2(\text{SO}_4)_3$ aluminum sulfate,
 - 5-30% of $\text{Al}(\text{OH})_3$ aluminum hydroxide,
 - 0.5-10% of mineral acid,
 - 0-10% of alkanolamine,
 - 15 - 0-5.0% of fluidizer,
 - 0-20% of stabilizer,
- in aqueous solution.

As mineral acid, preference is given to using
20 phosphoric or boric acid, but it is also possible to use other mineral acids having a similar action, e.g. nitric acid, sulfuric acid, etc.

Diethanolamine is advantageously used as alkanolamine. Polycarboxylates, particularly advantageously Sika
25 ViscoCrete®, in particular Sika ViscoCrete® 20HE are advantageously used as fluidizers.

Silica sol is advantageously used as stabilizer.

Particularly advantageous setting and curing
30 accelerators consist essentially of (in % by weight):

- 30-50% of $\text{Al}_2(\text{SO}_4)_3$ aluminum sulfate, in particular 40-45%, and/or
- 5-20% of $\text{Al}(\text{OH})_3$ aluminum hydroxide, in particular 10-17%, and/or
- 35 - 0.5-8% of mineral acid and/or
- 0-5% of alkanolamine and/or
- 0.1-3.0% of fluidizer, in particular from 0.1 to 1.0%, and/or

- 0-10% of stabilizer.

It is also advantageous to add the mineral acid fraction of 0.5-10% as H_3PO_4 phosphoric acid and/or
5 H_3BO_3 boric acid. Particularly advantageous ranges are 1-5% of H_3PO_4 phosphoric acid and/or 0.5-3.0% of H_3BO_3 boric acid.

A number of samples of an accelerator according to the
10 invention were produced in the above-described ranges. The composition of these samples is indicated in the following examples.

Example 1:

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7.60 kg of aluminum hydroxide $\text{Al}(\text{OH})_3$ are added to a solution of 22.50 kg of aluminum sulfate with water of crystallization $\text{Al}_2(\text{SO}_4)_3 \times 14 \text{H}_2\text{O}$ in 17.06 kg of water H_2O at 70-80°C. 1.14 kg of a phosphoric acid solution
20 H_3PO_4 (75%), 2 kg of a silica sol (10% solids content) and 1.70 kg of a corrosion inhibitor, viz. a 90% solution of diethanolamine, are subsequently added to the resulting solution and this mixture is stirred for half an hour.

25 The stability of this mixture was at least 70 days.

Example 2:

7.60 kg of aluminum hydroxide $\text{Al}(\text{OH})_3$ are added to a
30 solution of 22.50 kg of aluminum sulfate with water of crystallization $\text{Al}_2(\text{SO}_4)_3 \times 14 \text{H}_2\text{O}$ in 14.86 kg of water H_2O at 70-80°C. 2.84 kg of a phosphoric acid solution H_3PO_4 (75%), 0.50 kg of polycarboxylates, e.g. Sika ViscoCrete® 20HE which is a high-performance fluidizer,
35 and 1.70 kg of a corrosion inhibitor, viz. a 90% solution of diethanolamine, are subsequently added to the solution obtained and this mixture is stirred for half an hour.

The stability of this mixture was at least 70 days.

Example 3:

5 8.00 kg of aluminum hydroxide $\text{Al}(\text{OH})_3$ are added to a solution of 22.50 kg of aluminum sulfate with water of crystallization $\text{Al}_2(\text{SO}_4)_3 \times 14 \text{H}_2\text{O}$ in 16.56 kg of water H_2O at 70-80°C. 1.14 kg of a phosphoric acid solution H_3PO_4 (75%), 0.10 kg of boric acid H_3BO_3 and 1.70 kg of
10 a corrosion inhibitor, viz. a 90% solution of diethanolamine, are subsequently added to the solution obtained and this mixture is stirred for half an hour. The stability of this mixture was at least 70 days.

15 **Example 4:**

8.10 kg of aluminum hydroxide $\text{Al}(\text{OH})_3$ are added to a solution of 20.60 kg of aluminum sulfate with water of crystallization $\text{Al}_2(\text{SO}_4)_3 \times 14 \text{H}_2\text{O}$ in 21.00 kg of water
20 H_2O at 70-80°C. 0.30 kg of boric acid H_3BO_3 is subsequently added to the resulting solution and this mixture is stirred for half an hour. The stability of this mixture was at least 70 days.

25 **Example 5:**

8.00 kg of aluminum hydroxide $\text{Al}(\text{OH})_3$ are added to a solution of 21.00 kg of aluminum sulfate with water of crystallization $\text{Al}_2(\text{SO}_4)_3 \times 14 \text{H}_2\text{O}$ in 20.00 kg of water
30 H_2O at 70-80°C. 1.00 kg of boric acid H_3BO_3 and 0.50 kg of polycarboxylates, e.g. Sika ViscoCrete® 20HE which is a high-performance fluidizer, are subsequently added to the solution obtained and this mixture is stirred for half an hour.
35 The stability of this mixture was at least 70 days.

From 0.1 to 10% by weight of the accelerator of the invention can be added to the hydraulic binder.

To determine the effectiveness of the accelerator of the invention from Examples 1 to 5, 6% of the accelerator from the above examples was in each case mixed into portland cement and penetrometer values were determined. The following table shows the penetrometer values together with the time required in each case to reach strengths of 200 g, 600 g and 2200 g. These penetrometer values were determined using a needle having a diameter of 3 mm and a test apparatus from RMU.

A sample of portland cement without accelerator was used as comparison and the penetrometer values for the same sample composition when the accelerator was left out without replacement and when the accelerator was replaced by a corresponding amount of water were determined.

Penetrometer value for	200 g	600 g	2200 g
Example 1	5 min	7 min	15 min
Example 2	6 min	8 min	16 min
Example 3	6 min	9 min	20 min
Example 4	7 min	14 min	40 min
Example 5	12 min	20 min	55 min
Sample without accelerator	450 min	485 min	540 min
Sample without accelerator but with equivalent amount of water	490 min	522 min	579 min

The accelerators prepared as described in Examples 1 to 5 thus gave solutions which display satisfactory acceleration values and remain stable for a sufficiently long time.

The accelerators of the invention can also be used for hydraulic binders other than cement, e.g. blended cements, lime, hydraulic lime and plaster of Paris and also mortar and concrete produced therefrom.

Of course, the invention is not restricted to the example presented and described. The accelerators present in aqueous solution can also be used in dried form, e.g. after drying by means of a generally known
5 spray drying process. The dried powder obtained in this way, which is readily soluble in water, is dissolved in water before use and then used in the same way as the liquid accelerator. The samples prepared as described in Examples 1 to 5 can also be produced in a
10 temperature range from room temperature RT to 90°C, but preferably in a range from 50 to 80°C.